Pathways for the Oxidation of Sarin in Urban Atmospheres

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Abstract

The nerve agent sarin has recently been deployed by terrorists in a major city. The molecule is volatile and made its way to many victims by passing as vapor through a highly reactive medium. Here we estimate rates and pathways for the removal of gas phase sarin from a generalized urban atmosphere. Only information from the open scientific literature is used. By structure reactivity comparisons with the organophosphorus pesticides, hydroxyl radical hydrogen abstraction may occur in as little as one hour. Decomposition of side chains after hydroxyl attack leads to organic oxygenates which preserve the phosphonofluoridate and so toxicity. The aqueous aerosol surface is contacted in minutes and offers access to a range of dissolved nucleophiles. Substitution displaces the fluoride leaving group, giving safe phosphoric acid analogs. Because of uncertainties in the electron distribution and in aqueous decay mechanisms, the time constants must be viewed as lower limits.

Keywords: Aerosol; hydroxyl; nerve agents; ozone; sarin; terrorism; urban environment

1 Introduction

Hoaxes and a few actual incidents have raised the concern that terrorists will release chemical or biological warfare agents into the atmospheres of world cities [1,2]. Nerve agents are especially potent chemical toxins. One of the most volatile among them, sarin, was the substance disseminated in the well publicized Tokyo subway attack [3]. A dozen deaths and thousands of hospitalizations were attributed to the standard cholinergic symptoms [4].

Although the nerve gases can be dispersed as droplets, sarin is also effective in the vapor phase [4,5]. In Tokyo, it was permitted to evaporate from open containers. During transit to victims and surfaces, the gas phase molecule was subject to oxidative and heterogeneous decomposition within an urban air mass. Mechanisms and rates for such decay are poorly understood. However, removal from the atmosphere may significantly impact casualty and deposition patterns.

In the present work, we draw on information in the open scientific literature to delineate sarin degradation pathways in the urban environment. Limits are also placed on several key reaction time constants.

We begin our development by noting that military/defense oriented discussions of atmospheric nerve agent oxidation have focused on low pollutant, battlefield regimes. Research on the closely related organophosphorus pesticides indicates that the major reactants likely in cities are hydroxyl radical, ozone and the aqueous aerosol. Rate constants for gas phase reactions are estimated based on pesticide data and volatile organic structure-reactivity relationships. Urban air quality data provide reactant concentrations and particle surface areas. Aerosol contact frequencies are computed microphysically. In a concluding discussion section, we argue that the gas phase reactions of sarin might profitably be studied through standard techniques of atmospheric chemistry. Other chemical or biological agents will be distributed as particles so that mechanisms for deposition are relevant as well.

The present text is condensed from an extensive report of the same title on file at Los Alamos National Laboratory [6]. Over two hundred literature citations are provided, from the fields of nerve agent and pesticide chemistry, urban air quality and tropospheric chemistry, and international terrorism/urban security.

2 Gas Phase Processes

The organic molecule which goes by the common name sarin is in fact o-isopropylmethylphosphonofluoridate, with the shorthand structure $CH_3P(O)(F)OCH(CH_3)_2$ [5]. It is often acknowledged that the isopropyl side chain on the molecule will be subject to standard oxidation sequences in the atmosphere [1,7,8]. The hydroxyl radical is the primary initiator of decay for saturated hydrocarbons. Following hydrogen abstraction, a variety of oxygenated intermediates will form from the sarin precursor [9]. Since some will retain the phosphonic acid core responsible for cholinesterase inhibi-

tion [10], toxicity may remain. Danger will persist until the phosphorus-fluorine bond has been broken; fluoride is the leaving group involved in enzyme binding. The family of phosphorus acids constitute a safe, stable product set.

References to the sarin hydroxyl reaction can be found in the available defense literature, but they are often oblique [7,8]. Battlefield conditions in recent decades have tended to be remote/pristine from the atmospheric standpoint. In urban air, concentrations of major oxidants such as the hydroxyl will be larger by an order of magnitude or more [9]. The organophosphorus pesticides are structurally related to the nerve agents [10,12] and offer considerable guidance on decay rates and mechanisms. Their oxidation has been studied relative to agricultural areas adjacent to U.S. cities. Much of the work has focused on metroagroplexes in the state of California.

Table 1 summarizes laboratory data for the rate of hydroxyl attack on a series of semisymmetrical pesticide analog molecules [13]. The radical OH is best modeled as an electrophile, and inductive shifts in electron density toward an organic group will speed hydrogen abstraction. The effect is demonstrated in the listing; the thion ester forms are less stable. In Table 2 the trimethyl phosphate value is placed in the context of classic organic structure reactivity relations [9,14,15]. Extrapolation downward along the columns indicates that the central hydrogen of the sarin isopropyl could react as rapidly as 10^{-11} cm³ molecule⁻¹ s⁻¹. Statistically, abstraction from the terminal methyls could be competitive.

The strongly electronegative fluoride substituent complicates estimates substantially. Phosphonofluoridate has not been studied in the structure-reactivity context. The fluorine atom will draw electrons from other portions of the carbon skeleton and slow abstraction. The rate constant 10^{-11} is thus an upper limit. Ozone reacts with the pesticides only slowly, at $<3 \times 10^{-19}$ cm³ molecule⁻¹ s⁻¹ [13]. The point of interaction may be the thion/oxon but is not well determined. A zeroth order assumption is that sarin behaves similarly.

Tropospheric ozone concentrations have been extensively studied [9]. In remote areas, values fall as low as 10 ppbv. In major cities in the developed world, 100 ppbv are not uncommon during pollution episodes. Enclosed, developing cities may experience hundreds of parts per billion quite regularly [16]. Even under the most polluted circumstances, the ozone reaction requires several days. Hydroxyl is short lived and so difficult to measure directly. Photochemical models suggest that concentrations are on the order of 10^6 radicals cm⁻³ in remote air masses, but exceed 10^7 cm⁻³ in dirty urban air [9]. The values crest at local noon. The sarin lifetime with respect to hydrogen abstraction may be as little as an hour under peak photochemical conditions. The nitrate radical survives in urban air at night. However, we can surmise once again by comparison with the other OP species that reaction with NO_3 will be slow [13]. By this logic, hydroxyl reaction with isopropyl hydrogens is the major sarin loss channel. A suite of aldehydes, ketones and other oxygenates will appear early in the oxidation sequence as intermediate products of organic group decay.

3 Aerosol Processes

The rate at which vapor phase species contact aerosol surfaces may be modeled microphysically based on theories of gas kinetics and diffusion control [17]. Summary results are shown in Figure 1 for a reaction probability of 0.1. In the urban particulate system available area maximizes in the accumulation mode, between roughly 0.1 and 1 micron in radius. Number densities are on the order of 10^3 to 10^4 particles cm⁻³, and lie toward the higher end of the range in polluted regimes. Sarin released into city air will reach the aerosol in on the order of one minute. The molecule is very sensitive to nucleophilic reactions. Substitution onto the enzyme active site is the mechanism of cholinesterase inhibition [10]. Hydrolysis is in general expected to be rapid in moist environments. Identification of the phosphoric acid derivatives is considered evidence of deployment [11,1]. At moderate to high relative humidity, the urban aerosol may be characterized as a mixture of roughly equal parts geological (crustal) material, soot (secondary or-

Table 1: Rate constants for gas-phase reactions of OH radicals with a series of organophosphorus compounds at 297K

Organophosphorus Compound	k(cm³ molecule⁻¹ second⁻¹) $10^{-13} \times k_{OH}$
$(CH_3O)_3PO$	7.37 ± 0.74
$(CH_3O)_2P(O)SCH_3$	9.29 ± 0.68
$(CH_3S)_2P(O)OCH_3$	9.59 ± 0.75
$(CH_3O)_3PS$	69.7 ± 3.9
$(CH_3O)_2P(S)SCH_3$	56.0 + 1.8
$(C_2H_5)_3PO$	55.3 ± 3.5
$(CH_3O)_2P(O)N(CH_3)_2$	31.9 + 2.4
$(CH_3O)_2P(S)N(CH_3)_2$	46.8 ± 1.4
$(CH_3O)_2P(S)NHCH_3$	232 + 13
$(CH_3O)_2P(S)NH_2$	244 ± 9

Table 2: Partial (per hydrogen) abstraction rate constants (10^{-12} cm³ hydrogen⁻¹ s⁻¹) for the attack of hydroxyl radical on organic molecules with different substituents X

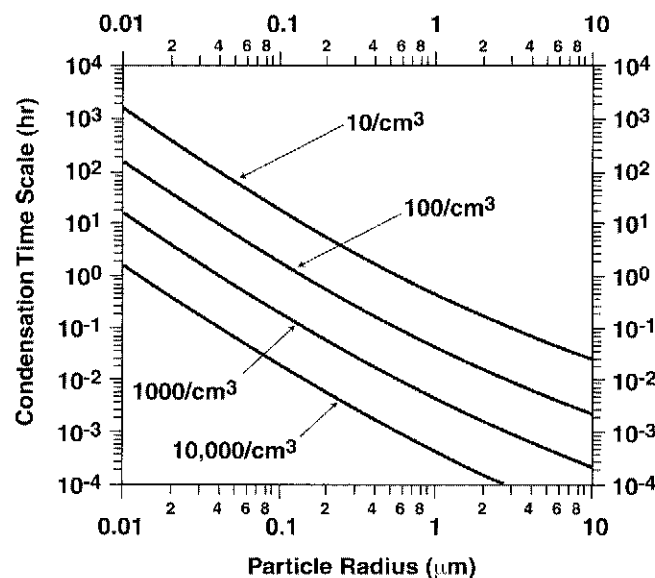|	X Group					
	ONO₂	H	CH₃	OH	OCH₃	OP(O)(OCH₃)₂
HCH₂-X	0.01		0.05	0.3	0.5	0.7
RCH₂-X	0.01	0.05	0.50	1.2		
R₂CH-X	0.13	0.50	2.0	5.0		
CH₃CHX-R	0.02	0.05	0.05			
CH₃CH₂CHX-R	0.08					

Fig. 1: Characteristic time for removal of vapor to particle as a function of radius and aerosol number concentration

ganic oxygenates and elemental carbon), and high ionic strength ammonium sulfate/nitrate solutions. Nucleophiles abound. Sarin decay may occur rapidly in/on particle surfaces.

4 Discussion

The logic we develop suggests that in an urban milieu the nerve gas sarin would begin vapor phase oxidation in an hour and aerosol dissolution/decay in a minute. The time constants are lower limits. If they are approached, distributions in a terrorist release zone are determined chemically to a large extent. Indoors, sprinkler devices might be installed to remove agent quickly from air through reactive scavenging. Uncertainties in our estimates could be significantly reduced through standard laboratory gas phase and heterogeneous kinetics experiments. The rate of attack by hydroxyl and of sarin uptake at the aqueous interface could be measured. Reports on sarin kinetics are rare in the open literature and the results difficult to translate to the real atmospheric situation [6,19]. We have not attempted to search military/defense sources. High agent concentrations near the point of release may in fact suppress hydroxyl and saturate the nucleophilic substitution potential. Detailed modeling of the interaction between decomposition and dilution would be of interest [20].

The other nerve agents (e.g. soman, VX and tabun) are relatively involatile and so are likely to be distributed as droplets during a terrorist attack [5]. Biological weapons are necessarily particulate [1]. In these cases, sedimentation and deposition may dominate. Study of removal from urban air becomes an extension of standard atmospheric aerosol research. However, the micro (building or street canyon) scale will be the focus. Varied surface textures and angles must be considered, and the interactions of deposition and turbulence will be complex. We plan in the near future to apply available knowledge of urban and pesticide aerosol deposition to these high resolution issues.

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